

P&G

*Photochemical
Approaches to Decontamination*

Joint Services Scientific Conference on Chemical
and Biological Defense Research.

November 20th, 2003

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Overview

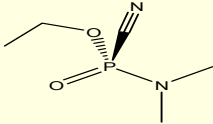
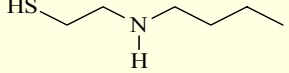
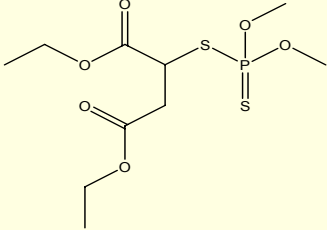
- Six month project to:
 - evaluate singlet oxygen, superoxide and hydrogen abstraction for reaction with chemical weapons simulants.
 - Identify principal products and reaction pathways.
 - Determine approximate conversion to products.
 - Evaluate reaction confined to a surface.

P&G Photochemical Technology

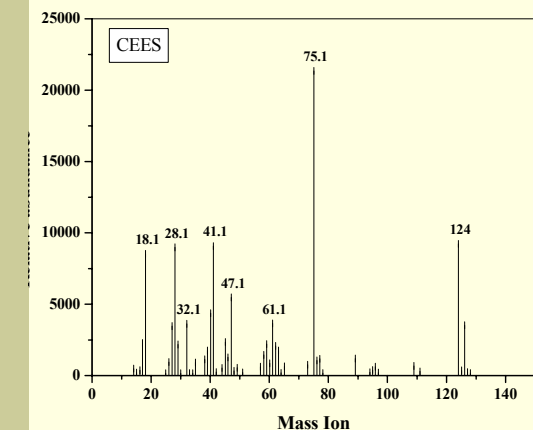
Background

- Visible through near infrared (200 nm – 800 nm).
 - Colorless systems.
- Low power requirement, typically 0.01 – 0.1 W/m²
- Energy and electron transfer control
- Organic and inorganic
- Sensitizers for:
 - Singlet oxygen
 - Superoxide
 - Hydrogen abstraction
 - Redox

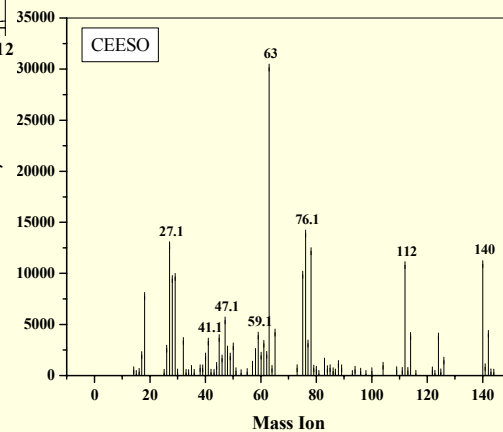
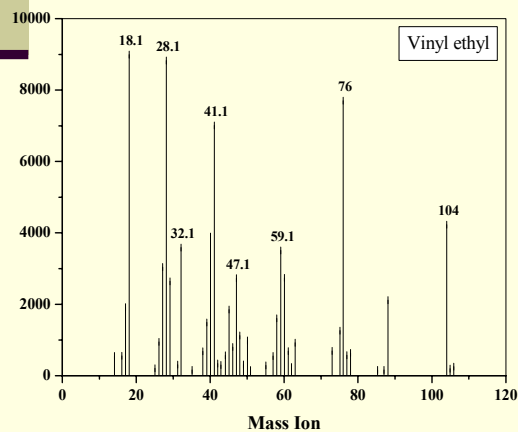
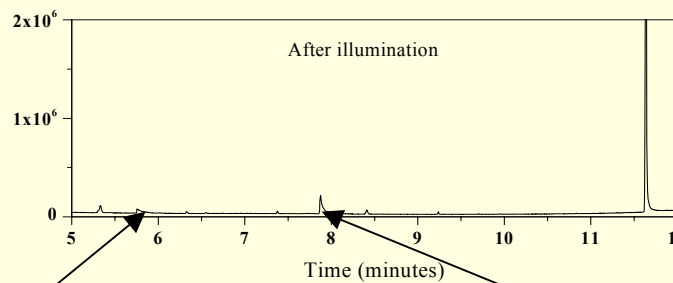
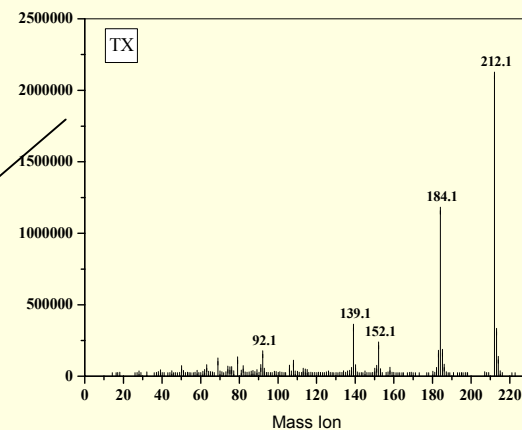
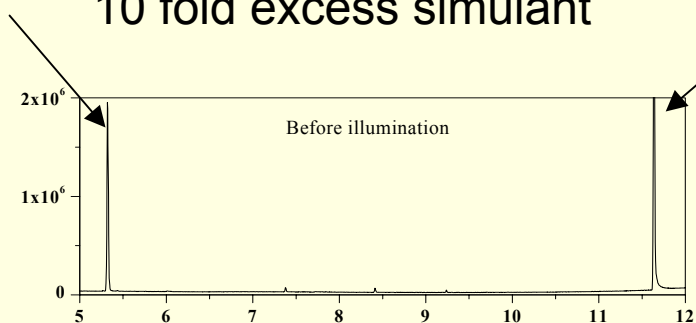
Chemical Weapon Simulants

CW Agent	Simulant
<p>Sarin (GB)</p> $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{F})-\text{O}-\text{CH}(\text{CH}_3)_2$	<p>Dimethyl methylphosphonate (DMMP).</p> $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{CH}_3)_2$
<p>Soman (GD)</p> $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{F})-\text{O}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_2$	<p>Ethyl dichlorophosphate</p> $\text{EtO}-\text{P}(=\text{O})(\text{Cl})_2$
<p>Tabun (GA)</p> 	<p>Diethyl chlorophosphate</p> $\text{EtO}-\text{P}(=\text{O})(\text{Cl})(\text{OEt})$
<p>VX</p> $\text{C}_2\text{H}_5\text{O}-\text{P}(=\text{O})(\text{CH}_3)-\text{S}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_2\text{CH}_3)_2$	<p>2-(Butylamino)ethanethiol</p> 
	<p>Malthion</p> 
<p>Mustard gas</p> $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{Cl}$	<p>2-Chloroethyl ethylsulfide</p> $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_3$

Photochemical Technology Product Identification

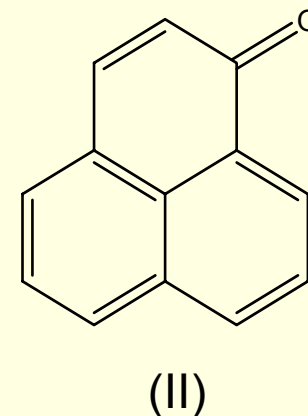
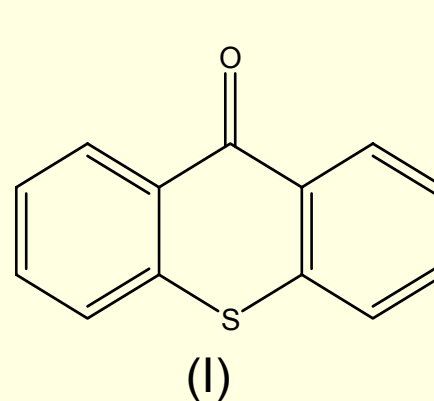
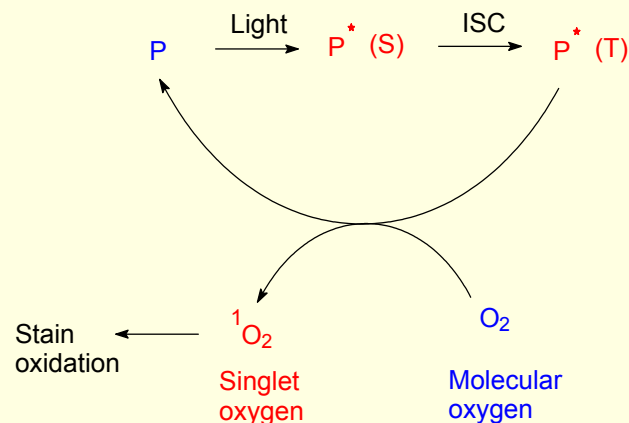


10 fold excess simulant

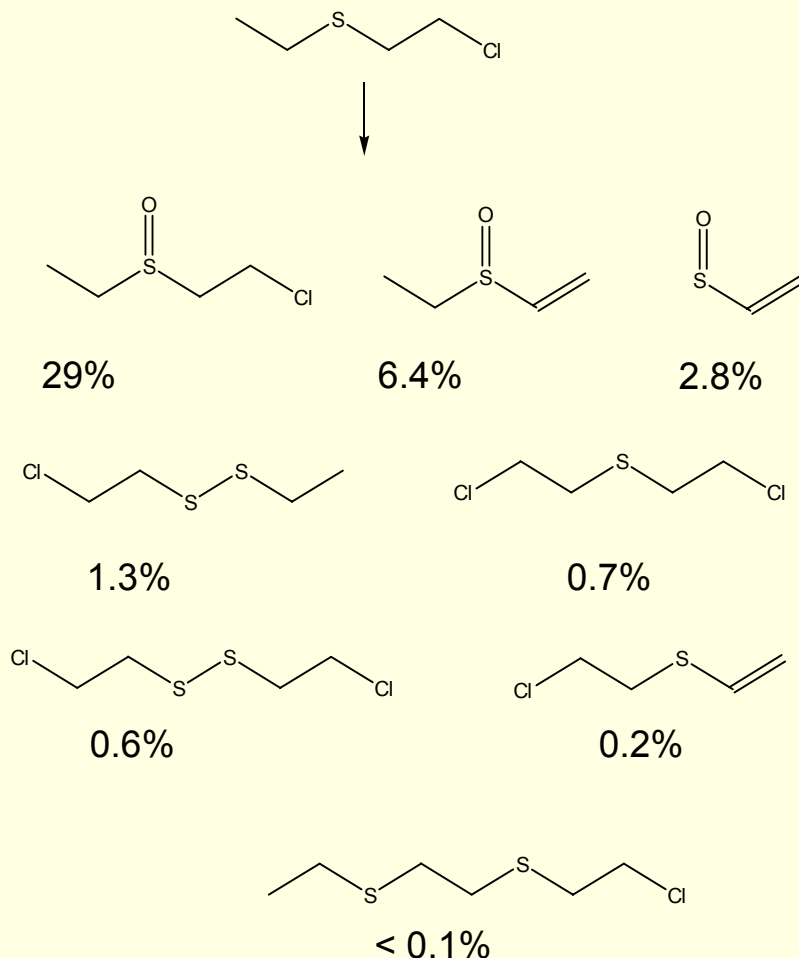


Photochemical Technology: Singlet Oxygen

- Photosensitized activation of oxygen to form singlet oxygen
- Very short lived:
 - 5 μ s in water
 - 30 μ s in THF
- Can be generated at most wavelengths (250nm – 750nm)
- Examples:
 - Thioxanthone (I)
 - Perinaphthenone (II)
 - Phthalocyanines
- Powerful electrophilic oxidant

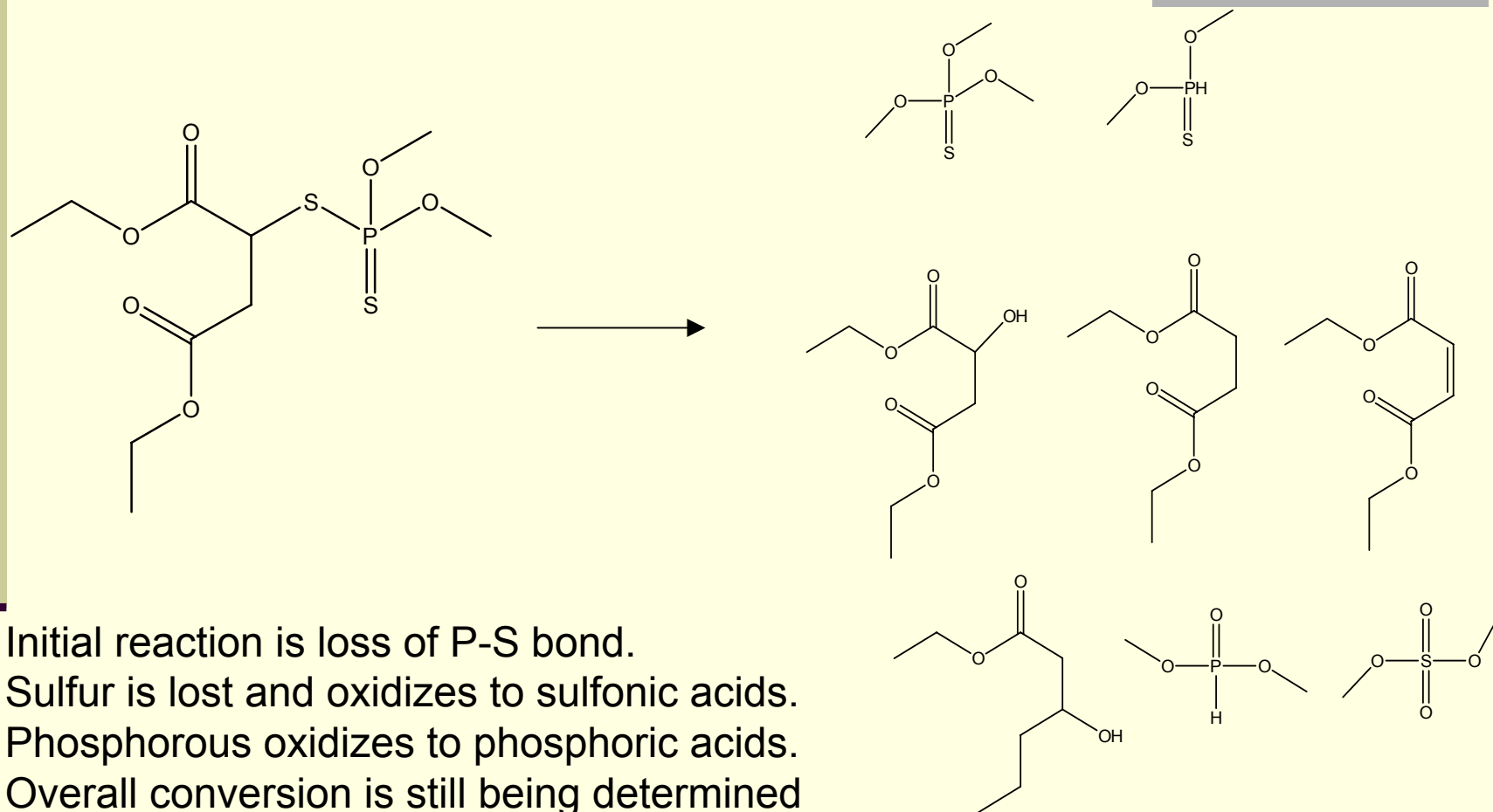


Singlet Oxygen reaction with Half Mustard



- Initial reaction is oxidation of the sulfur and/or HCl elimination.
- Carbon sulfoxide bond cleaves and coupling (radical) products are generated.
- Electrophilic nature of oxidant prevents sulfone formation.
- Overall ~90% conversion to products in 15 mins.
- Surface coatings and neat CEES gives ~80% removal in 60 minutes.

- Initial reaction is loss of P-S bond.
- Sulfur is lost and oxidizes to sulfonic acids.
- Phosphorous oxidizes to phosphoric acids.
- Overall conversion is still being determined

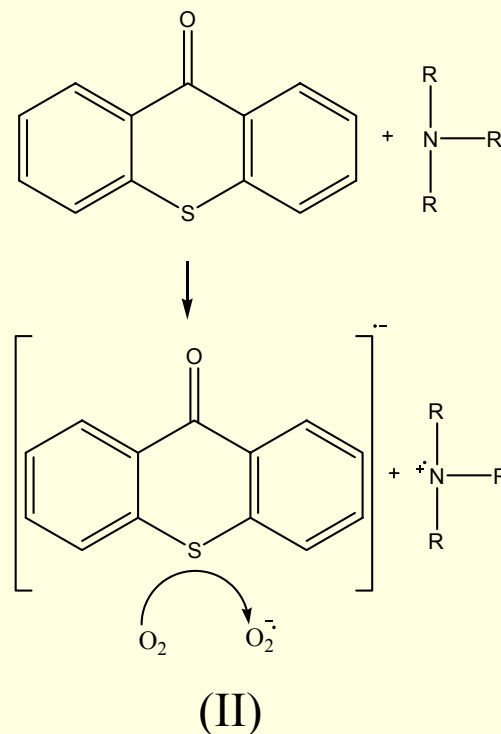
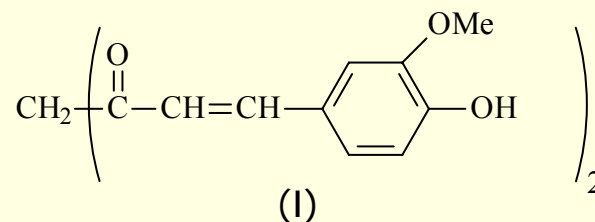


Singlet Oxygen reaction with Phosphonates (Sarin/Tabun/Soman)

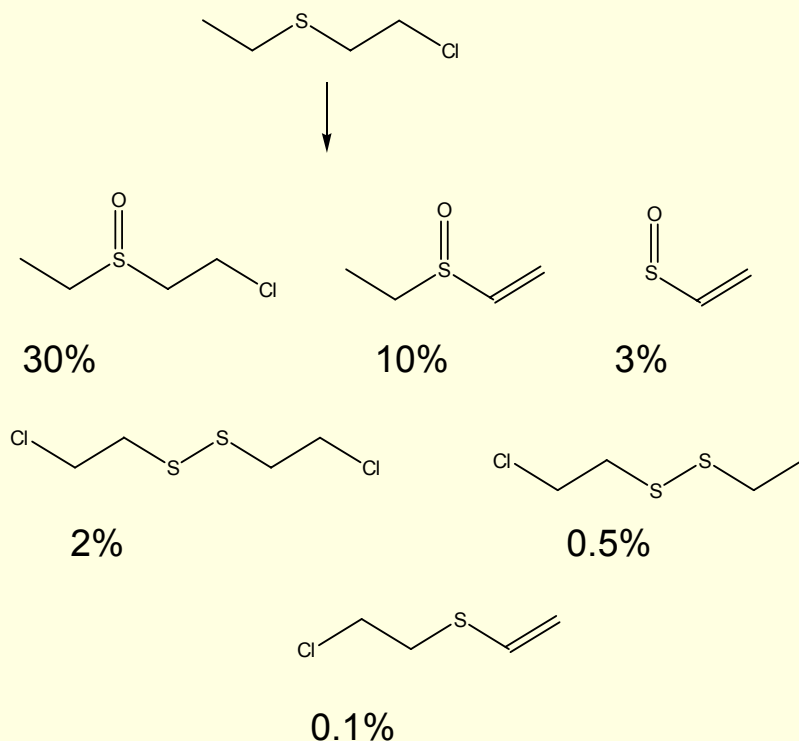
- No reaction was found between singlet oxygen and any of the G agent simulants.
- G agents are based around a 'fully oxidized' phosphorous so unlikely to be reactive with electrophilic oxidant.
- Singlet oxygen could be used to generate hydroperoxides or similar to provide reactivity with G agents.

Photochemical Technology: Superoxide

- Photosensitized electron transfer.
- Superoxide is longer lived (seconds to minutes) than singlet oxygen species
- Can be generated at most wavelengths (300nm – 700nm).
- Examples
 - Curcumin (I)
 - Thioxanthone + amine/amide (II)
- Powerful oxidant and base.



Superoxide Reaction with Half Mustard



- Reaction products are similar to singlet oxygen
 - Oxidation of sulfur and/or HCl elimination
 - Cleavage of carbon sulfoxide bond and coupling products.
 - Greater HCL elimination due to basicity of superoxide.
- Overall ~90% conversion to products in 15 minutes
- Surface coatings and neat CEES gives ~50% removal in 60 minutes.

Superoxide Reaction with Malathion (VX)

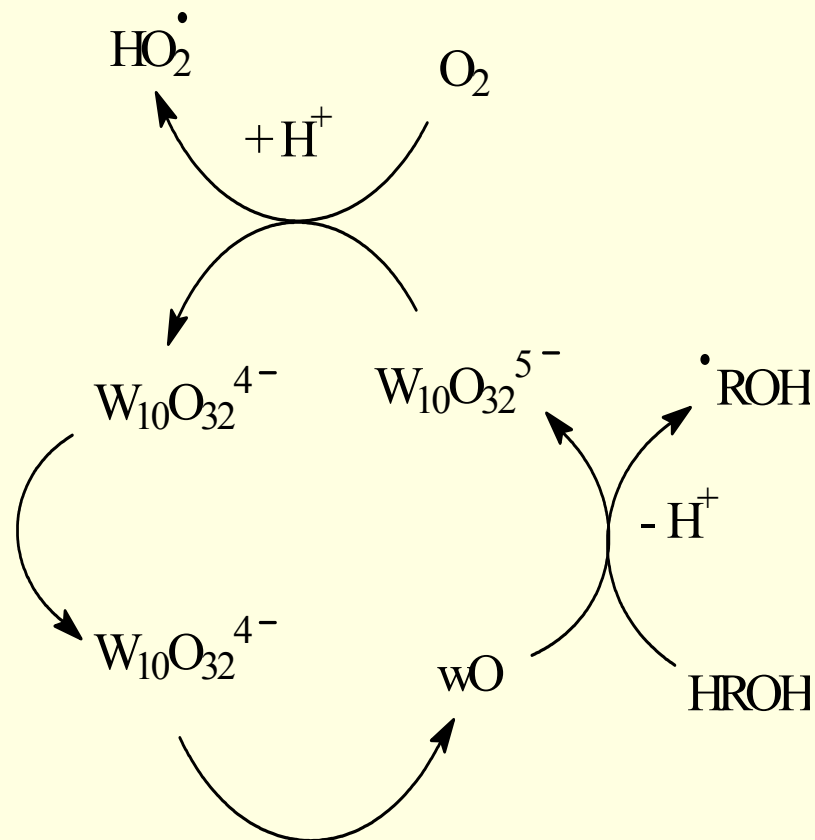
- Superoxide systems tried to date have led to loss of Malathion but products could not be identified (product and sensitizer overlap).
- Other sensitizer systems being evaluated.

Superoxide Reaction with Phosphonates (Sarin/Tabun/Soman)

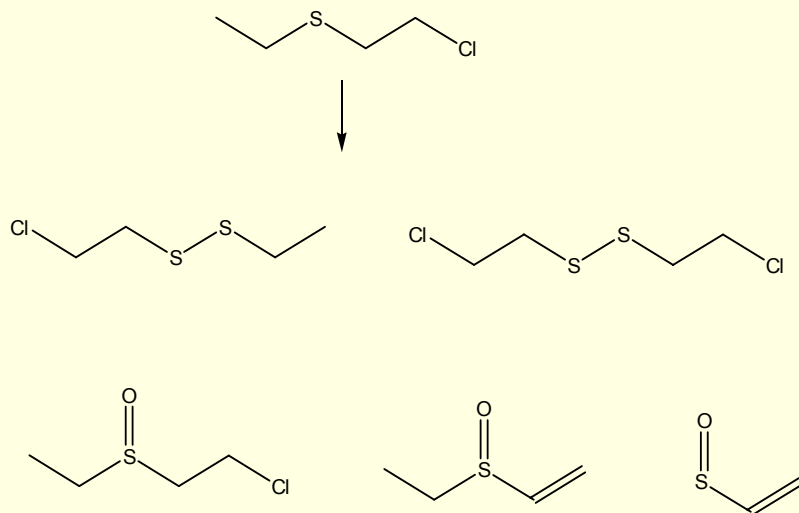
- Initial results for dimethyl methyl phosphonate indicate that G agents are probably not reactive towards superoxide
 - Consistent with literature: Aguila et al *J. Phys Chem. A* **2001**, 105, 7834
- Ethyl dichlorophosphate and dichloro ethylphosphate are still under evaluation.

Photochemical Technology: Hydrogen Abstraction/Redox

- Careful sensitizer selection or structural manipulation provides redox or hydrogen abstraction
- Examples:
 - Polyoxometallates
 - Ketones
 - Semiconductors
- Powerful reductants, oxidants, and biocides.

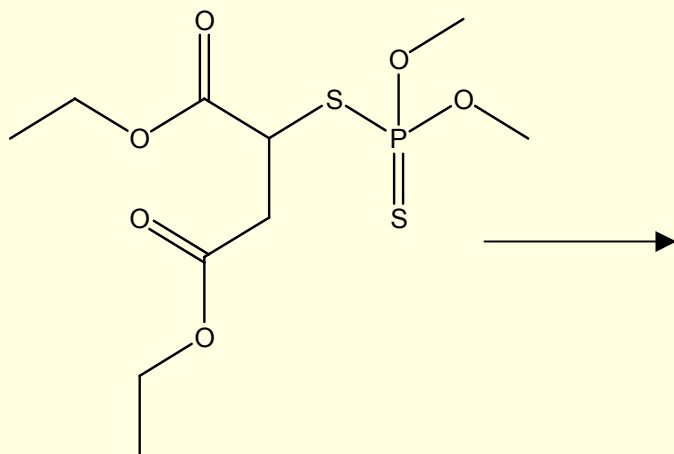


Hydrogen Abstraction with Half Mustard

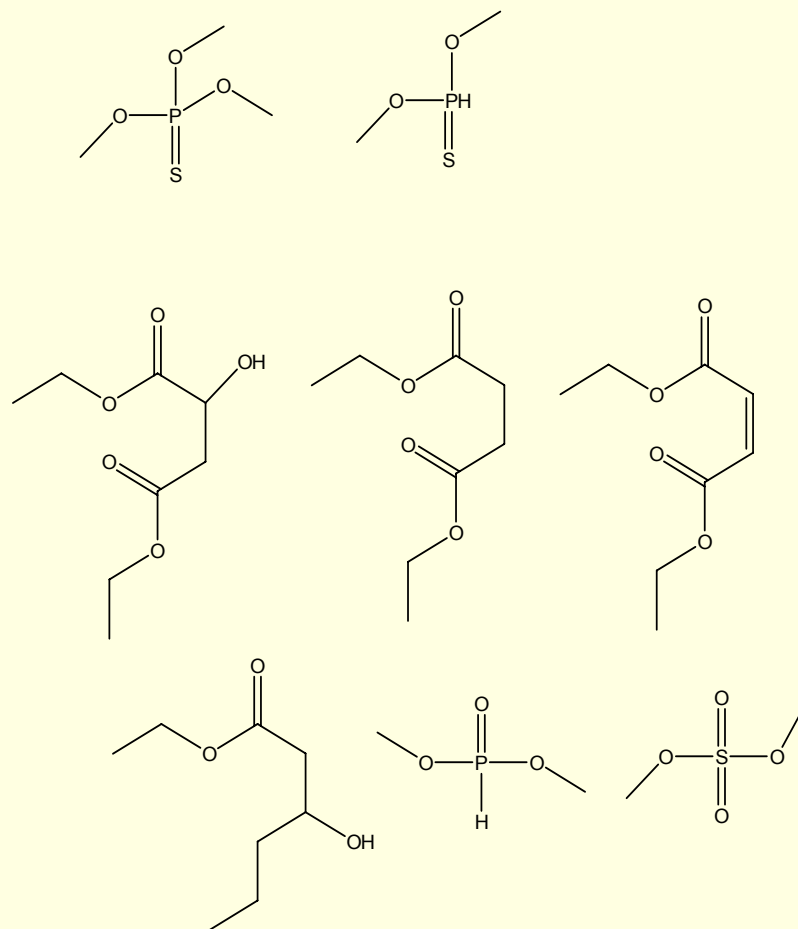


- Coupling products dominate as compared to singlet oxygen and superoxide where oxidation of the sulfur predominates.
- Polyoxometalate:
 - High concentration ~90% < 5 mins.
 - Sensitive to conditions (attacks solvents etc.)
 - Product analysis run at high substrate concentration and short time.
 - Surface reaction gives ~50% in 60 minutes.
- Ketone:
 - ~90% in 15 mins.
 - Similar product distribution to polyoxometalate.

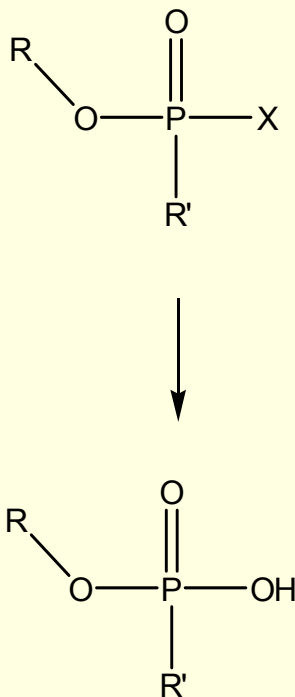
Hydrogen Abstraction with Malathion (VX)



- Initial reaction is loss of P-S bond.
- Sulfur is lost and oxidizes to sulfonic acids.
- Phosphorous oxidizes to phosphoric acids.
- Overall conversion is still being determined



Hydrogen Abstraction with Phosphonates (Sarin/Tabun/Soman)



R = Me or Et
R' = Me or OEt or Cl
X = Cl or OMe

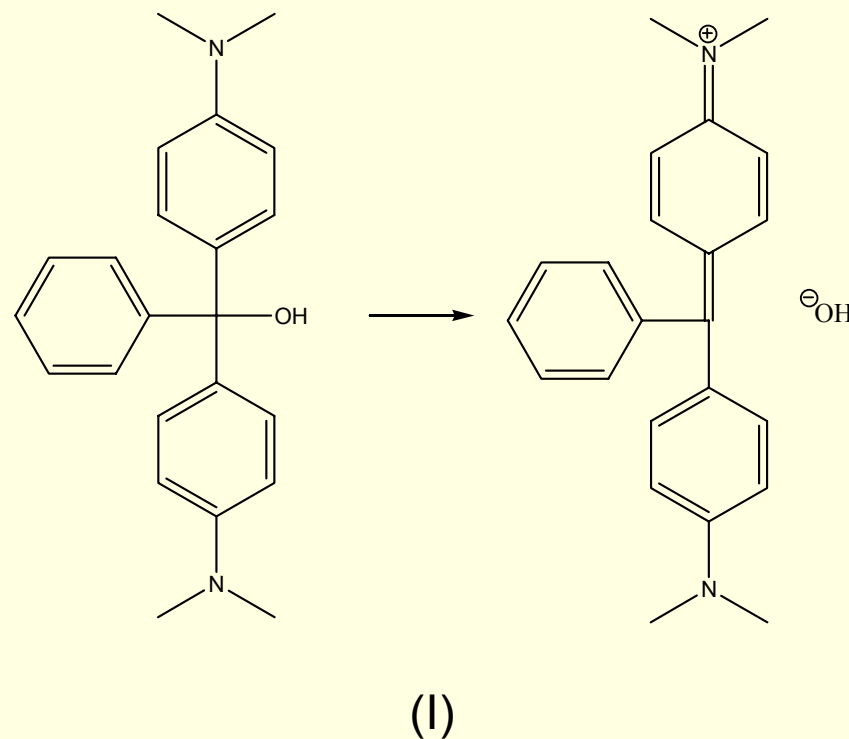
- Reaction appears to lead to rapid loss of either a halogen or methoxy group.
- Groups appear to continue to be lost and phosphate is likely end product.
- Conversion to products:
 - ~ 90% in < 6 minutes with polyoxometalate and DMMP.
 - ~ 50% in 30 minutes for chlorophosphates*

* Preliminary results

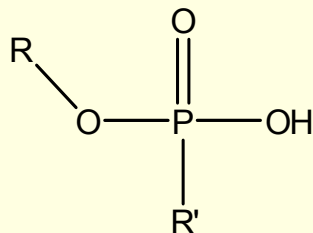
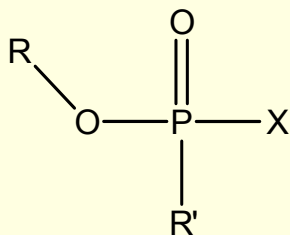
Photochemical Technology

Photobase

- Generates basic moieties such as amines, hydroxyl etc.
- Can generate base in aprotic media.
- Sensitizers between 250nm and ~450nm.
- Examples:
 - Triphenyl carbinol
 - Malachite green (I)
- Strong base and nucleophile.



Photobase and Phosphonates (Sarin/Tabun/Soman)



- Reaction apparently leads to loss of halogen or methoxide.
- Initial evaluation did not determine if further reaction occurs.

R = Me or Et

R' = Me or OEt or Cl

X = Cl or OMe

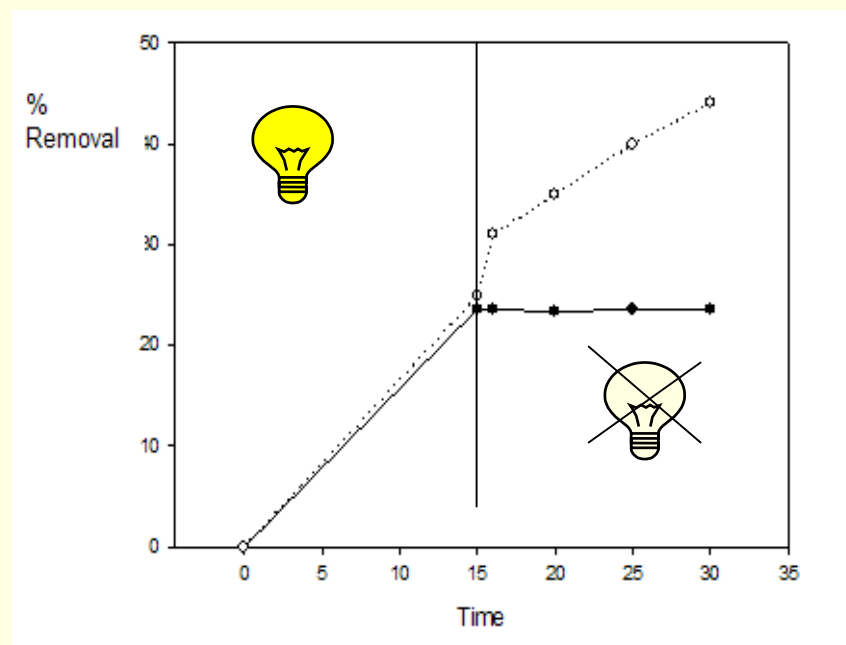
Photochemical Technology Review

Photochemistry	CWA Simulant					
	DMMP (Sarin)	Ethyl dichloro phosphate (Sarin/Tabun/ Soman)	Diethyl chloro phosphate (Sarin/Tabun/ Soman)	Malathion (VX)	Butylamino ethanethiol (VX)	Chloroethyl ethyl sulphide, CEES (Mustard)
Singlet Oxygen	✗	✗	✗	✓	✓	✓
Superoxide	✗			✓	✓	✓
Hydrogen Abstraction	✓	✓	✓	✓	✓	✓
Photobase		✓		✓	✓	

- **Phototechnology can provide a viable approach to the generation of reactive surfaces for decontamination.**
 - Singlet oxygen and superoxide are rapidly effective against simulants for VX and mustard.
 - Trapping all or part of these as hydroperoxides would likely provide activity on G agents.
 - Hydrogen abstraction is effective against all simulants tested.
 - More coupling reactions observed in addition to breakdown.
 - Photobase hydrolysis provides an alternative to hydrogen abstraction on G agents

What Happens at Night?

- Photochemistry in the Dark:
 - Light activated generation of actives.
 - Continues to be reactive from seconds to hours after activation.
 - Activation takes seconds to minutes.
 - Actives include singlet oxygen, superoxide, radicals (H-abstraction) + other oxidants.
 - Functions in both aqueous and non-aqueous (e.g. silicone, perfluorinated solvent etc.) environments.



Phototechnology Advantages

- High activity against wide range of potential chemical weapons threats
 - Also will be effective against toxic industrial chemicals.
- Strong biocidal activity especially for superoxide and hydrogen abstraction.
 - Possible 'one stop shop' for chemical and biological weapons agents.
- Robust across all surfaces.
 - Can be used on sensitive equipment.
 - Likely safe on all materials.
- Aqueous or non-aqueous media.
- Photoactivation provides for decon in the dark!
- Can be used for decontamination or as reactive surface.
- Activity of coating can be easily checked using UV/Vis or fluorescence detection.

Potential Applications

- Equipment Decontamination (wher light available).
- Sensitive equipment decontamination and decontamination solution cleanup.
- Decontamination powder/solution;
 - Photoactivate or use ambient light
 - area clean up,
 - equipment decon.
 - Personnel decon
 - Wound sterilization
- Surface reactive systems for sustained decontamination and cleaning.
 - Incorporation in paints and surface coatings.
 - User applied film for field use/reapplication.
 - In-use activity can be monitored by UV/vis or fluorescence.
 - Color change on reaction possible
 - In addition to potential activity for C&BWA could have more mundane application for keeping surfaces clean and antimicrobial e.g., tenting, clothing.
- Water purification
 - Lightweight polymer beads for water purification without tainting the water.
 - Coating on the interior of drinking utensils
- Air purification.
 - Packed bed stable until needed

Acknowledgements

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- Dr. James Tinlin and Mr. Bill Mueller.
- **Thank you for your time**